

The Nature of Lithium Perchlorate and Gallium Chloride Salt Effect in Cycloaddition Reactions.

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Abstract: Comparing the acceleration effects of (4+2)-, (3+2)- and (2+2)-cycloaddition reactions in the presence of the salts of two types: gallium chloride in inert solvents and lithium perchlorate (LP) in diethyl ether (DE) it was observed that in the presence of GaCl_3 the acceleration effect is approximately the same (10^4 times) for the studied reactions, while in LPDE medium for the same reactions strong increase (up to 10^4 times), weak increase or even decrease of the rate and equilibrium constants take place even with the common dienophile depending on the nature of the second reagent. It was suggested that the acceleration effect of cycloaddition reactions in the presence of such Lewis acids as aluminum, gallium or boron halides is due to the sharp increase of π -acceptor properties of dienophiles and therefore increasing energy of orbital interaction, whereas LPDE medium demonstrates strong stabilization of static and/or dynamic polar forms and favors reactions with charge control. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

The special interest to the investigation of organic reactions in salt solutions¹⁻⁸ is determined by the considerable increase of the rate of even those processes which have traditionally been considered to be low sensitive to the effects of the medium^{9,10} as well as by the possible change of the direction of the reactions.^{4,11,12} Current literature describes a number of examples with the easier course of reactions in LPDE medium. In the presence of LP under mild conditions and with high yield were obtained new cyclobutane adducts^{11,12} which are sometimes hard to reach in common solvents.

The considerable acceleration of the Diels-Alder reaction is observed when water is used instead of organic solvents.^{2,3} An even greater acceleration effect of cycloaddition reactions is observed when these reactions are performed in inert solvents in the presence of such Lewis acids as AlHal_3 , GaHal_3 and BHal_3 where the rate of reaction increases up to 10^6 times.¹⁰ The formation of stable n, ν -complexes between of dienophiles and these salts was shown.^{10,13,14} The sharp increase of the electrone affinity energy of activated dienophiles was concluded from the comparison of the changes of the charge transfer band energy of their π, π -complexes with hexamethylbenzene: 0.7-1.1 eV and 1.0-1.25 eV for maleimides activated by GaCl_3 and by AlCl_3 respectively.¹⁴

Some physical properties of LPDE solutions (electric conductivity, viscosity, density, partial molar volumes, vapor pressure and the composition of complexes) have been studied in the broad range of the salt